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Heavy metals in aerosol samples from the Eastern Pamirs collected 2004–2006

Guangjian Wu [a,*], Baiqing Xu [a], Tandong Yao [a,b], Chenglong Zhang [a], Shaopeng Gao [a]

[a] Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100085, China
[b] State Key Laboratory of Cryospheric Science, CAREERI, Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT

This study measured the concentration of heavy metal elements in atmospheric aerosol samples collected between July 2004 and April 2006 at a remote site on Mt. Muztagata (38°17'N, 75°01'E, 4430 m), in the Eastern Pamirs. Inductively coupled plasma mass spectroscopy (ICP–MS) results show that the air at Muztagata contains low concentrations of As and heavy metal elements (Cr, Ni, Cu, Zn, Cd, Pb, and Bi), comparable with those in the Arctic — far lower than in heavily populated or industrialized areas. Observed enrichment factor (EF) values greater than 10 for those elements suggest partly anthropogenic sources. Seasonal variations in the concentrations of Zn, Cd, Pb, Bi, and As resemble those of crustal Al, with greater concentrations during the summer but lower ones in winter. Our results reveal that the background atmosphere in remote inner Asia is only weakly affected by anthropogenic pollution, and demonstrate that high heavy metal concentrations occur during summer but with greater EF values during the winter. The air mass back-trajectory analyses suggest that pollution from West Asia, Central Asia, and South Asia are the main possible source areas that contribute to the heavy metals in aerosols at Muztagata.

1. Introduction

During long-range transport, dust aerosols carry large quantities of mineral particulates as well as anthropogenic air pollution to remote regions (Gao et al., 1992). Among airborne pollutants are trace elements such as Cd, Pb, Sb, and Zn associated with suspended particulates from a variety of pollution emission sources. The largest anthropogenic emissions of atmospheric trace metals appear to occur in Asia. These exceed the emissions of other continents, and also show an increasing trend (Pacyna and Pacyna, 2001). In many sites in East Asia, analyses of aerosol samples have shown that the heavy metal content increased sharply over its natural background due to anthropogenic emissions (Hashimoto et al., 1994). Previous studies on anthropogenic pollution in a dust storm at Beijing showed that the pollutants (including perhaps As) may have come from either pollution sources along the dust storm pathway or (for contaminants such as Zn and Cu) from local pollution sources (Zhuang et al., 2001).

Heavy metal pollutants have also been found in the remote and highly elevated regions of the Tibetan Plateau (Huo et al., 1999; Xiao et al., 2001; Cong et al., 2007). Human activities, such as fuel combustion and the metallurgical industry, in the countries of Central and West Asia emit heavy metals to the atmosphere, which the Westerlies can transport eastward to Mt. Muztagata in the Eastern Pamirs (Li et al., 2006). One year of continuous aerosol sampling in the central Tien Shan has revealed both local natural and anthropogenic pollution sources in southern Kazakhstan (Hoornaert et al., 2004). Some aerosol composition studies have been done in the westernmost areas of China, such as at Aksu (Zhang et al., 2003), Tashkurgan (Taxkorgan) and Kara Kul Lake (Makra et al., 2002). The Kafirnigan Valley Desert Dust Experiment in southeast Tajikistan, carried out in September 1989, studied chemical and physical properties of the dust and showed that anthropogenic elements were weakly enriched (Andronova et al., 1993). Those studies provide valuable basic data to help understand the properties of dust over the Pamirs and Central

* Corresponding author.
E-mail address: wugj@itpcas.ac.cn (G. Wu).

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Asia, including anthropogenic heavy metals. However, long-term aerosol sampling is required to provide reliable measurements of their background concentrations and to fully understand the seasonal to annual variations of heavy metals in the atmosphere.

In order to gain information on heavy metals in the atmospheric environment over Eastern Pamirs, we carried out continuous aerosol samplings at high altitude on Mt. Muztagata over a period of nearly 2 years (2004–2006). The weekly sampling intervals provide sufficient material to analyze the trace elements for detailed information on the atmospheric composition and anthropogenic pollution in this region. This paper presents the results of trace element analyses of those aerosol samples. The main purposes of this work were to (1) provide the background concentrations of heavy metals in the atmosphere and expand the database for remote regions in inner Asia, (2) evaluate the degree to which anthropogenic heavy metal pollution is contaminating the atmospheric environment of the Pamirs, (3) determine the seasonal variations of heavy metal elements, including their concentrations and enrichment factors, and (4) determine the possible pollution source areas.

2. Sampling and analysis

2.1. Aerosol sampling

Beginning in 2002, our research group carried out field atmospheric observations and sampling at 4430 m on the west slope of Mt. Muztagata (Muztagh Ata, 38°17′ N, 75°01′ E), in the Eastern Pamirs (Fig. 1). The sampling location is a very long way from the big cities (about 150 km southwest of Kashgar, a middle city, and about 50 km north of Tashkurgan, a small county town). The sampling site is about 3 km from a residential area and 8 km from the Kashgar–Tashkurgan road where there are a few shepherd and livestock activities. From June 2004 to December 2005 continuous aerosol samples were collected with an open-faced filter holder according to the method described by Sun et al. (1998). From June 2005 to April 2006, we used a newly designed total suspended particulate (TSP) impact sampler to collect aerosols. All the sampling was performed on the terminal moraine of a glacier on a western slope of Mt. Muztagata. Because the two sampling methods differ and there may be some discrepancies between their records, we use the terms 'OFF (open-faced filter)' and 'TSP' to refer to the samples collected by the old and new sampler, respectively. Parallel sampling was completed during an overlapping period in order to compare the OFF and TSP records, and those results are discussed below (see discussion in Section 3.1).

All the aerosol samples for both the OFF and TSP samplers were collected on Teflo™ filters (Pall Corporation, Ann Arbor, Michigan)) with a diameter of 47 mm and pore size of 1.0 μm. The filter holders were protected with a rainproof cover. Electric power to run the vacuum pumps was supplied by a solar panel system with a lead-acid storage battery. The pumps were equipped with an automatic air flow meter (Taihe Automation Control and Instrument Corporation, Tianjin, China), calibrated with an accuracy of ±1.5%. The flow rate of the TSP vacuum pump was set at an average of 20 L (under local pressure). This was done in consideration of the low aerosol background. The air volume for each sample was calibrated to standard sea level pressure (1013 mbar) using the average pressure value (which was automatically measured every 20 min) during each sampling period. The duration of each sampling period was set to 7 days, with a few

Fig. 1. Locations of aerosol sampling sites (black dots) at and surrounding Mt. Muztagata.

Table 1
ICP–MS measurements for detection limits and blank filter concentrations; Al, As, and heavy metal elements of reference material GSS-8; and the precision ($n=6$) for a TSP aerosol sample.

		Detection	Blank filter	GSS-8 reference material			Precision (%)
	Unit	Limit ($\pm 3\sigma$)	Concentration	Measured	Certified	Accuracy (%)	($n=6$)
Al	ng g^{-1}	0.104	8.53	62500	63106	−0.96	0.73
Cr	ng g^{-1}	0.085	0.134	68.98	68	1.44	1.11
Ni	ng g^{-1}	0.063	<0.000[a]	32.26	31.5	2.41	1.21
Cu	ng g^{-1}	0.069	<0.000	25.31	24.3	4.16	1.17
Zn	ng g^{-1}	0.277	1.85	71.29	68	4.84	1.3
As	ng g^{-1}	0.018	<0.000	12.75	12.7	0.39	4.3
Cd	pg g^{-1}	3.32	<0.000	0.113	0.13	−13.08	2.52
Pb	ng g^{-1}	0.01	0.015	19.65	21	−6.43	0.76
Bi	pg g^{-1}	4.53	<0.000	0.31	0.3	4.33	5.27

[a]Means the concentration was below the detection limit.

occasions of 10–14 days. After sampling, the filters were changed by our research group members and were individually placed into pre-cleaned polyethylene wide-mouth bottles for transport and subsequent analysis.

2.2. Inductively coupled plasma mass spectrometry (ICP–MS) analysis

Inductively coupled plasma mass spectroscopy results provide the elemental composition of aerosol samples (e.g., Arimoto et al., 2004; Senaratne and Shooter, 2004). In this study, the quantitative elemental analyses of the Muztagata aerosol samples (filters) were performed using ICP–MS (Thermo X-7, Thermo-Elemental Corporation) at the Institute of Tibetan Plateau Research, CAS. Filters were dissolved with suprapure HNO_3 (CMOS grade, J.T. Baker Inc.) and HF (BVIII grade, Beijing Institute of Chemical Reagents) at 150–190 °C in polytetrafluoroethylene screw-top bombs. After digestion, the dust on the Teflo™ filters was totally dissolved. The Chinese national reference material GSS-8 (loess from Luochuan, Chinese Loess Plateau, Chinese National Research Centre for CRMs) was digested and measured following the same method for quality control, especially the digestion efficiency. Duplicate analyses of GSS-8 show very good agreement with its certified values (with accuracy better than ±13%), indicating that this method is reliable for measurement of trace elements. The precision of ICP–MS for a TSP aerosol sample is better than 5.5% for those heavy elements (Table 1).

The ICP–MS analyses provide data for some major crustal elements (such as Al, Sc, Ti, Mg, Fe), heavy metal elements

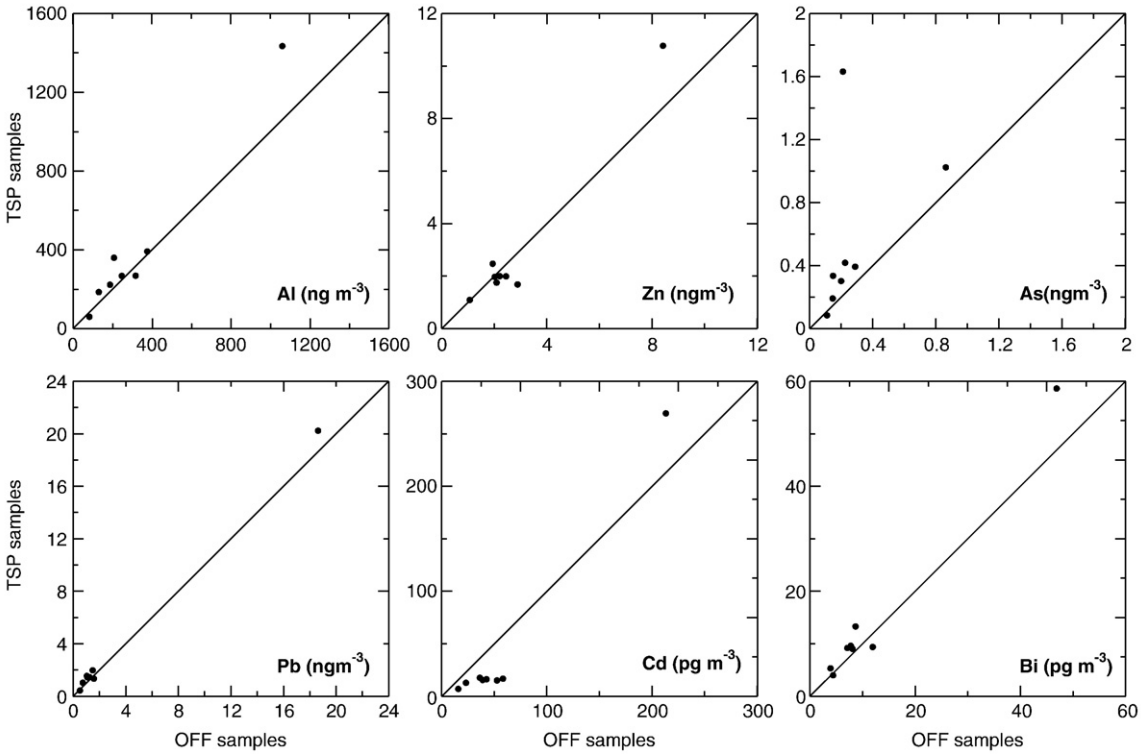

Fig. 2. Comparison of OFF and TSP data sets in the overlapping sampling period.

Table 2
Statistics of concentrations of Al, As, and heavy metal elements at Muztagata, both the OFF and TSP aerosol samples.

		OFF					TSP				
	Unit	*n*	Arithmetic mean	SD	Geometric mean	Range	*n*	Arithmetic mean	SD	Geometric mean	Range
Al	ng m^{-3}	61	841.6	1098.9	485.29	81.3–6368.5	36	509.2	776.8	244.29	31.1–3395.1
Cr	ng m^{-3}	59	1.98	2.87	1.16	0.11–19.57	34	1.93	1.50	1.36	0.13–6.91
Ni	ng m^{-3}	61	1.07	1.63	0.62	0.06–11.66	35	1.01	0.80	0.73	0.08–3.19
Cu	ng m^{-3}	61	1.18	0.93	0.92	0.93–4.69	35	0.94	0.77	0.69	0.12–3.36
Zn	ng m^{-3}	56	3.38	2.82	2.53	2.82–14.55	32	3.58	3.14	2.59	0.55–12.62
As	ng m^{-3}	50	0.60	0.54	0.40	0.54–2.46	34	0.46	0.47	0.30	10.08–1.83
Pb	ng m^{-3}	61	2.32	2.80	1.54	0.31–18.63	36	2.23	3.89	0.97	0.08–20.23
Cd	pg m^{-3}	60	39.01	45.21	25.10	4.86–229.84	33	30.24	52.37	14.94	2.14–269.34
Bi	pg m^{-3}	61	19.21	19.82	12.76	2.66–101.62	33	14.43	16.45	9.06	2.32–66.97

(such as Cr, Ni, Cu, Zn, Cd, Pb, Bi), and other toxic elements (such as As). The blank filters were also digested and measured, following the same procedures as for the aerosol samples, showing very low concentrations. The blank filter values for Al, Cr, Zn, and Pb concentrations (Table 1) are minor relative to the lowest concentration values of TSP aerosol samples, with percentages of 9.7%, 20.8% (2.2% to the median), 33.5% (14.2% to the median), and 7.7%, respectively. The blank background values were subtracted from the measured results. In some samples, some heavy metal elements were not detected because their concentrations in the solutions were too low or data were not generated due to quality constraints.

3. Results and discussions

3.1. Heavy metal concentrations

Results of the two sampling methods during the overlapping sampling period need discussions. Here we show the comparison between the OFF and TSP data sets from October 7 to December 10, 2005 with continuous sampling. The OFF and TSP samples show a good similarity in their concentration trends for the crustal elements (Al) and some heavy metals (such as Bi). However, there are still some notable discrepancies between the OFF and TSP samples for some trace elements (such as As, Fig. 2) which result from the different sampling methods. In this paper we interpret their concentration separately without giving a conversion from the OFF to TSP data sets.

Concentrations of heavy metal elements show large variability from June 2004 to April 2006. The average, standard deviation (SD), median, minimum (Min) and maximum (Max) values of heavy metal concentrations in the Muztagata aerosol are listed in Table 2. Results from other sites are also listed in Table 3 for the purpose of comparison. Heavy metals in airborne dust over the Eastern Pamirs have very low concentrations. Cr, Ni, Cu, Zn, As, and Pb elements in air have average concentrations of several nanograms per cubic meter, while Cd and Bi have tens of picograms per cubic meter. These levels are of the same magnitude as found at other remote locations, such as the central Tien Shan (Hoornaert et al., 2004), Nam Co, inner Tibetan Plateau (Cong et al., 2007), and Waliguan GAW station, northeastern Tibetan Plateau (Wen et al., 2001). However, aerosols in northern China, at Aksu, Zhenbeitai (Zhang et al., 2003), and Beijing (Sun et al., 2005), were found to have much higher heavy metal concentrations, generally more than one order of magnitude greater than at Muztagata, due to their proximity to more intense human activities. Previous studies have collected aerosol samples at Tashkurgan (3010 m, 50 km south of Muztagata) and Kara Kul Lake (3595 m, 22 km north of Muztagata) in the summer of 1994 (Makra et al., 2002). Although their sampling times were about 1.5–2 h and air volumes were about 1–3 m^3, those two samples also showed very low heavy metal concentrations. The Kara Kul Lake

Table 3
Concentration of As and heavy metal elements in TSP aerosol samples in Eastern Asia and Arctic.

		Muztagata	Tien Shan	Nam Co	Waliguan	Aksu	Zhenbeitai	Beijing[a]	Alert[b]	Arctic[c]
		Mean	Mean	Mean	Min–max	Mean	Mean	Mean	Mean	Mean
Al	ng m^{-3}	509.2	140	131	2110–3410	24,000	14,000	19,000	96	
Cr	ng m^{-3}	1.87	1.3	1		56	11	48		
Ni	ng m^{-3}	1.01	0.95	0.61		192	67	190		0.85
Cu	ng m^{-3}	0.94	0.56	0.6		112	44	170	1.8	
Zn	ng m^{-3}	3.28	1.8	2.2	9.5–26.3	42	28	570	4.6	1.9
As	ng m^{-3}	0.45	0.04		0.70–3.37	116	115	330		0.26
Pb	ng m^{-3}	2.23				159	64	250	1.6	3.3
Cd	pg m^{-3}	30.24						16,000		80
Bi	pg m^{-3}	14.43								
	Method	ICP–MS	EDXRF	PIXE	PIXE	PIXE	PIXE	ICP–AES	Multiple	AAS
	Source	This work	Hoornaert et al. (2004)	Cong et al. (2007)	Wen et al. (2001)	Zhang et al. (2003)	Zhang et al. (2003)	Sun et al. (2005)	Sirois and Barrie, (1999)	Shevchenko et al. (2003)

[a] During non-dust storm period.
[b] Sum of ten aerosol factors (components).
[c] Concentration during spring (maximum) time, Franz Josef Land, Russian Arctic.

aerosol sample indicated relatively high concentrations of Cr (8 ng m^{-3}), Ni (4 ng m^{-3}), Cu (6 ng m^{-3}), Zn (16 ng m^{-3}), which are several times higher than our Muztagata average. This difference results primarily from heavy metal concentrations remaining relatively high during summer compared to winter (see discussion in Section 3.3). The Tashkurgan sample had heavy metal concentrations several times to tenfold greater than those seen at Muztagata, because of its closer proximity to human activities and also because the sample was collected during the summer.

The elemental concentrations for heavy metals in the Mt. Muztagata aerosol, as well as in the Central Tien Shan and at Nam Co, are at low levels similar to those recorded in the remote Arctic, such as at Alert (Canadian arctic) (Sirois and Barrie, 1999) and Franz Josef Land (Russian Arctic) during spring (maximum) season (Shevchenko et al., 2003). This indicates that heavy metals have a background concentration in the atmospheric environment of the Eastern Pamirs, and pollution caused by human activities has little effect there.

3.2. Enrichment factor (EF)

Though the absolute concentrations for heavy metal elements are very low, their enrichment factors can be used to differentiate between natural and anthropogenic sources, and to assess the proportion of the anthropogenic contribution. Here we utilize Al as the reference element to calculate EF values, using the formula $EF = (X/Al)_{aerosol}/(X/Al)_{crust}$, where $(X/Al)_{aerosol}$ and $(X/Al)_{crust}$ represent the concentrations of an element (X) relative to Sc in the aerosol and crust (Taylor and McLennan, 1995), respectively. An EF value close to unity (less than 5) is considered to indicate a dominant input from rock and soil, while an EF value greater than 10 strongly suggests that the corresponding element originated mainly from other sources (Ferrari et al., 2004).

The Muztagata aerosol samples have EF values for dust-derived elements, such as Ca, Fe, Mg, Ti, Al, and Mn, of less than 1.5, showing that their compositions are very close to that of the upper continental crust and indicating a natural origin. Some heavy metal elements, such as Cr, Pb, Cd, and As, were found to be highly enriched (with EF values greater than 10) in the Muztagata OFF and TSP aerosol samples, indicating their additional non-natural sources (Table 4).

High EF values for those heavy metal elements in aerosols are also reported at different sites near the Eastern Pamirs, such as in the Tarim Basin (e.g., Aksu; Zhang et al., 2003), and remote sites in the central Tien Shan (Hooraert et al., 2004). Previous studies also show that aerosol samples collected at Tashkurgan and Kara Kul Lake have quite high EF values for Cr, Ni, and Cu (Table 4), and Zn during the summer season (Makra et al., 2002). The aerosol samples collected at Shaartuz (south Tajikistan) was found to be weakly enriched in anthropogenic elements compared with the local soil (Andronova et al., 1993). In an ice core drilled at an elevation of 7010 m near the summit of Mt. Muztagata, heavy metal elements, such as Bi, were measured and found to be enriched with high EF values (Li et al., 2006). Those data indicate that anthropogenic emissions provide a considerable contribution to heavy metals in the atmosphere over the Eastern Pamirs.

Heavy metal elements might have multiple potential natural sources, including mineral dust, forest fire ash, evaporated sea salt, volcanic activity, and continental and marine bioactivity (Nriagu, 1989). Because Muztagata is located in the center of Asia far away from the oceans, marine bioactivity and sea salt probably contribute very little to the high EF values in the aerosol. In addition, during 2004–2006, there was no volcanic activity around or near Muztagata. Furthermore, being situated in the westernmost part of China where the Westerlies commonly prevail at 500 hPa height in this area, anthropogenic pollution from industrialized and populated China will not often arrive at Muztagata. As there is no local pollution source near the Muztagata sampling site, these elements with high EF values must, at least partly, originate from distant anthropogenic sources.

There are three major anthropogenic sources of trace elements in the atmosphere: (1) stationary fossil fuel combustion is the major source of Cr, largely from coal combustion, (2) combustion of petroleum products provides the major source of Ni and V, and the combustion of leaded, low-leaded, and unleaded gasoline continues to be the major source of atmospheric Pb emissions, and (3) non-ferrous metal production is the largest source of atmospheric Zn, Cu, As, and Cd (Pacyna and Pacyna, 2001). Beside these three major sources, some heavy metals have specific sources. For example, waste incineration and the use of phosphate fertilizers in agricultural areas are major sources for Cd (Harmens et al., 2004). These different sources and their contributions will affect the concentrations and EF values of those heavy metal elements. Mining and metallurgical plants are one of the major sources of gaseous and heavy metal emissions into the atmosphere. Some countries in Central Asia have major metal-working industries. Kazakhstan pro-

Table 4
EF values for As and heavy metal elements in aerosol samples in Eastern Asia.

Site	Cr	Ni	Cu	Zn	As	Pb	Cd	Bi	Reference
Muztagata TSP	26.2	19.9	15.9	14.4	90.4	19.5	57.6	23.1	This work
Muztagata OFF	12.1	10.3	9.3	6.5	40.9	15.1	52.1	18.3	This work
Aksu	3.8	30	12	2	386	23			Zhang et al. (2003)
Tashkurgan	15.1		23	77.1					Makra et al. (2004)
Kara Kul Lake	56.7	49.6	59.6	55.9					Makra et al. (2004)
Nam Co	12.9	27.1	10.1	11.5	16.3				Cong et al. (2007)
Waliguan[a]				5	24.8				Wen et al. (2001)
Zhenbeitai	2.5	25	11	4.2	621	40			Zhang et al. (2003)
Beijing (Non-dust storm)	2.2	12.1	12	39	93	104	609		Sun et al. (2005)

[a]Fe as the reference element.

duces heavy metals, especially Cr, Zn, and Cd, accounting for 8.8%, 18.2%, and 3.5% of the world totals in 2005, respectively (British Geological Survey, 2007). This contributes, at least in part, to the high EF values of those three heavy metal elements in the Muztagata aerosol when the air mass moves southward to the Eastern Pamirs. The high EF values for those heavy metals show that anthropogenic sources contribute a significant proportion to the Muztagata aerosol samples.

3.3. Seasonal variations

Aerosol components have significant seasonal variations due to the periodicity of atmospheric conditions and of human activities. The content of heavy metals in aerosols over the seas of the Russian Arctic shows an annual variation with maximal concentrations of anthropogenic components during the winter/spring season (Shevchenko et al., 2003). The anthropogenic metals (such as Pb, Zn and Cu) exhibit

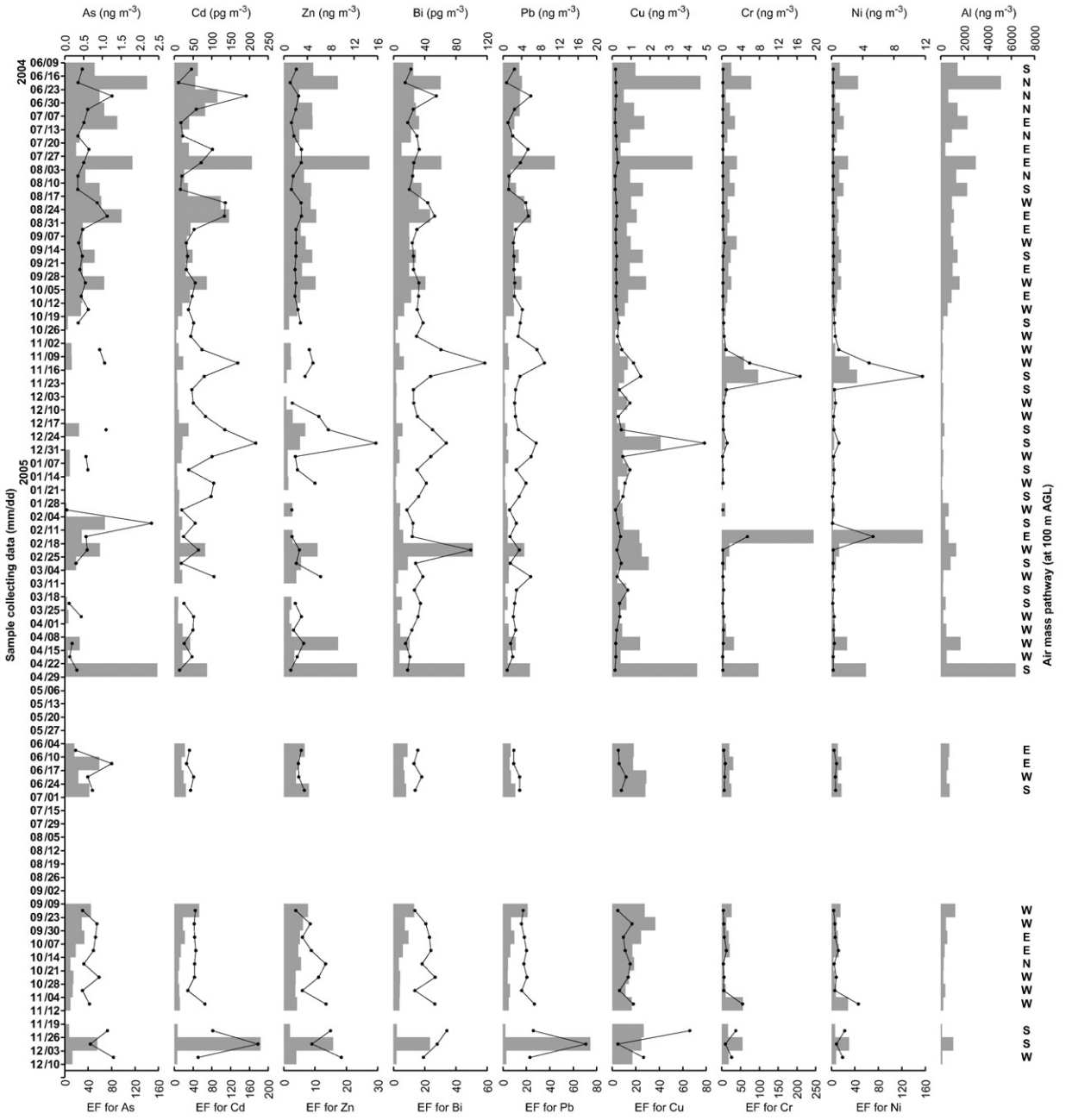

Fig. 3. Time series of heavy metal elements in Muztagata OFF aerosol samples. Grey bars indicate concentrations, while lines and dots indicate EF values. N (north), E (east), S (south), W (west) in the figure (for Al) means the air mass pathways calculated by the Hysplit back-trajectory model.

maximum concentrations in winter and minimum concentrations in summer at Alert, Canadian Arctic (Sirois and Barrie, 1999). However, the seasonal variations of heavy metal properties are complex. Whereas the lifetime of aerosols in the Arctic shows strong seasonality of aerosols associated with the lifetime of aerosols related to variations in transport and removal processes in the Arctic air mass (Barrie, 1986), the atmosphere at Muztagata responds quickly to anthropogenic pollution in source areas because of the relatively short pathway. Our weekly aerosol sampling at Muztagata recorded the temporal changes of heavy metals in the atmosphere. The aerosol samples show a clear seasonal variability in heavy metal concentrations and their EF values (Figs. 3 and 4).

As, Cd, Zn, Bi, and Pb show seasonal concentration features similar to Al, which showed high levels during summer (from July to October, 2004) while remaining at low levels from the end of October 2004 to February 2005. This suggests that they might have been controlled by the same atmospheric circulation and transport mechanisms as the dust aerosol, or they were attached to the dust particulates for long-range transport. During June, July and August 2005, the TSP samples show no obviously high heavy metal concentrations, but in September 2005, there are high concentrations of heavy metals. This indicates that their concentrations show large variability from year to year, and that the short sampling time is not sufficient to obtain the average levels.

In cases of high Al concentration, all the heavy metals also exhibit high concentrations but low EF values. The EF values also show temporal changes but do not resemble the concentration features, suggesting that the EF values are not strongly correlated with their absolute concentration. Generally, Zn, Bi, and Pb show similar seasonal EF features (as do their concentrations), indicating that greater EF values occur during the winter season when their concentrations are low. This suggests that the contributions from anthropogenic sources were much higher during the winter than the summer. The EF values for Cr, Cu and Ni show less variability, being mostly less than 20, but with a few instances when they rise by more than one hundredfold. The variations in EF values indicate that the proportion of anthropogenic contributions to heavy metals also changed temporally.

Both the OFF and TSP samples show that Cu, Zn, As, and Bi are tightly correlated with Al, showing that they were transported along with the dust, while Cr, Ni, Pb, and Cd seem to have the different transport dynamics to the dust. Some metals have the same source, such as the metallurgy and fossil fuel combustion, and can be tightly combined into element groups, such as Cr-Ni and Pb-Zn-Cd. Cr and Ni exhibit very similar variation features in their concentration profiles and are highly correlated ($R^2 = 0.98$ for OFF and 0.80 for TSP samples), suggesting that the two heavy metals might have the same sources, such as metallurgy and fossil fuel combustion. Cr and Ni in the atmosphere of the Eastern Pamirs show

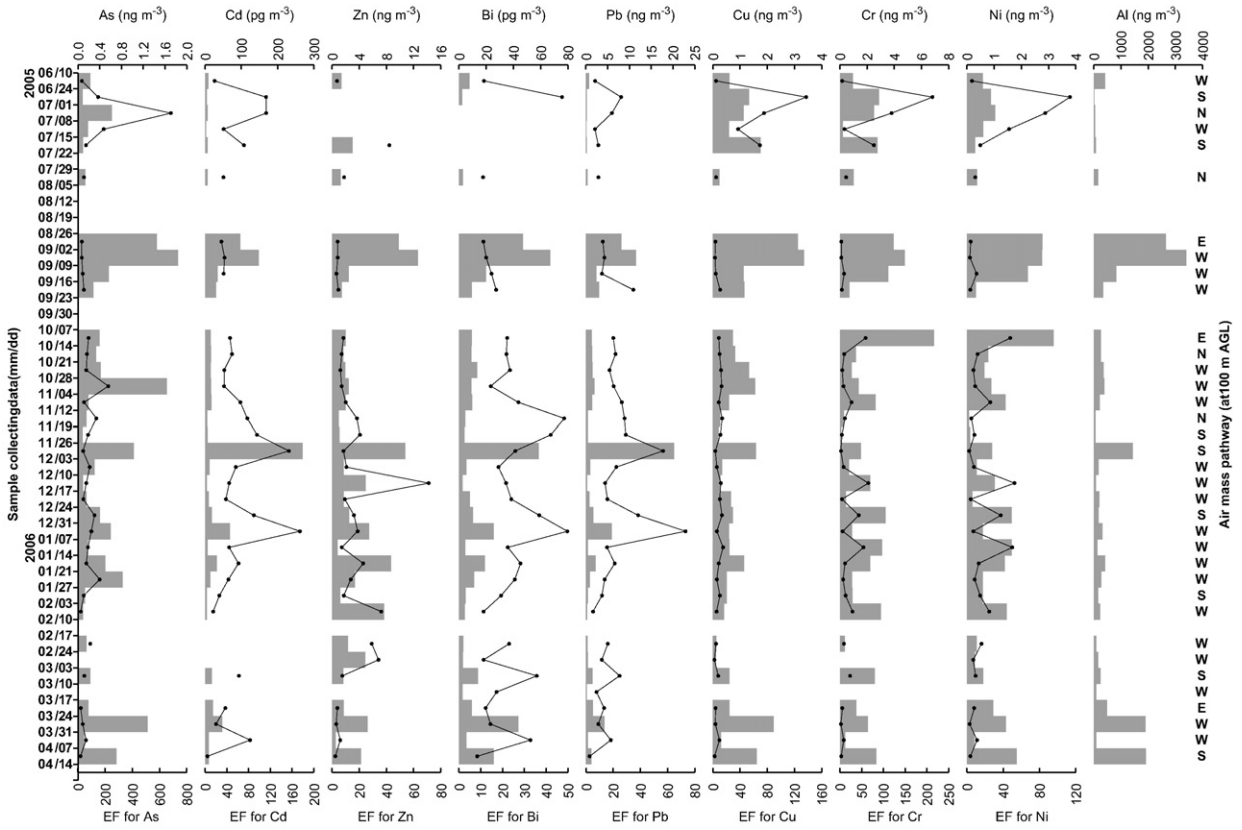

Fig. 4. Time series of heavy metal elements in Muztagata TSP samples. Symbols are the same as in Fig. 3.

Table 5
Comparison of mean and median metal concentrations according to different types of air mass trajectories.

Type	*n*	Al	Cr	Ni	Cu	Zn	As	Pb	Cd	Bi
		ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	ng m^{-3}	pg m^{-3}	pg m^{-3}
OFF E	12	1025.55	3.19	1.89	1.38	4.04	0.74	3.04	54.46	23.91
OFF N	6	1604.30	1.99	1.13	1.58	4.26	0.88	2.65	51.66	28.35
OFF W	25	526.19	1.31	0.71	0.89	2.57	0.38	1.75	28.95	15.56
OFF S	18	902.78	2.13	1.00	1.32	3.81	0.66	2.51	38.43	18.10
TSP E	3	1136.77	4.03	2.31	1.49	4.51	0.68	3.71	44.84	21.90
TSP N	4	134.41	1.25	0.57	0.61	1.31	0.31	0.62	8.82	5.57
TSP W	21	488.60	1.66	0.96	0.88	3.78	0.51	1.93	27.02	13.70
TSP S	8	515.42	2.11	0.86	1.04	3.52	0.34	3.25	42.74	17.09

no significant correlations to Al and other heavy metals, suggesting that their sources are different. Cr and Ni also show rather constant concentrations and relatively less variable EF values during the sampling period. Only occasionally do they have high concentrations or high EF values. As, which was mostly enriched, might have the same common source as Cu and, to a less extent, Zn. Cu has its unique temporal variations, with less variable concentration and not clear trends in EF values.

3.4. Back-trajectory analysis and possible pollution source areas

Though the back-trajectory results indicate the general airflow rather than the exact air mass pathways, they provide clues to possible anthropogenic source areas. We applied the Hysplit back-trajectory model (Draxler and Rolph, 2003) for multiple elevations for each aerosol sample. We modeled air mass tracks backward for 72 or 120 h before the end of each aerosol sampling. The near ground (100 m AGL) air masses show more east and south but fewer west pathways than the high level (1000 m AGL) ones. The total of 86 (there are 11 parallel samples in the overlapping sampling period between June 10 and December 10, 2005) air mass pathways (at 100 m AGL) can be categorized by four types: (1) from the east (E, from the Taklimakan Desert), (2) from the north (N, such as Kazakhstan and Kyrgyzstan), (3) from the south (S, such as Pakistan and India), and (4) from the west (W, including Tajikistan, Uzbekistan, Afghanistan, Iran, and further west). The number of cases for E, N, S, and W type pathways is 14, 9, 23, and 40, respectively.

We compared the air mass pathways with the heavy metal record and investigated some specific events with high heavy metal concentrations. The high concentration event that occurred between June 16 and June 23, 2004, corresponds to an air mass that came from the north; one between July 27 and August 3, 2004, came from west; one between April 22 and April 29, 2005, came from south. High EF value events could also occur with different air mass pathways. For example, high Cr and Ni EF values occurred with an air mass from the west traveling to Muztagata between November 19 and 26, 2004, and also with one from south between February 11 and 18, 2005. This suggests that high heavy metal concentrations and high EF values derive from a variety of pollution source areas around the Pamirs and the aerosols were well mixed along the pathway. The anthropogenic pollution from West Asia, Central Asia, and South Asia are possible source areas and any of them can cause high heavy metal concentrations or their EF values.

Air masses from the east are rare because high level Westerlies commonly prevail. Hence, pollutants from China contribute very minor amounts of heavy metals to the Muztagata region. During our sampling period, only two air mass tracks were found to have come from the Taklimakan Desert (occurring between July 7 and July 13, 2004, and between June 10 and June 17, 2005; Fig. 3). Those two events caused a little increase in As concentration, however, no obvious abnormal values in heavy metal concentrations and EF values, suggesting that anthropogenic pollution is minimal in the Taklimakan Desert at that sampling period. The back-trajectory analysis for the previously mentioned event that occurred between April 22 and April 29, 2005, shows that during this event, the air mass came from the south and passed over northwest Indian mountains, Kashmir, and Karakorum, which have even less pollution. That event exhibited high concentrations for the eight heavy metals, but small EF values.

Here we also calculate the mean of metal concentrations according to the different types by back-trajectory (E, N, W, and S) to show the impact of different source regions (Table 5). The heavy metals and As show no clear systematic correlation between their concentrations and air mass trajectories during the period of sampling. There still no significant relation that can be found between the pathways and EF values. For example, N type has the highest EF values for Ni, Cu, and As in TSP samples, while the N type does not show this characteristic and the EF for Ni, Cu, and As are the lowest ones is OFF samples. This is possibly, at least partly, due to the different sampling periods. The OFF and TSP samples show some differences in heavy metal absolute concentrations and their relative EF values with the same type of air mass pathway, suggesting that the heavy metals that were transported to the Eastern Pamirs vary year by year.

4. Conclusions

Continuous aerosol sampling for nearly 2 years (between June 2004 and April 2006) provides the first long-term information on heavy metals in the Eastern Pamirs atmosphere, and furthers our understanding of anthropogenic pollution in remote regions of inner Asia. Heavy metal elements were found to have a very low concentrations (comparable with remote Arctic regions), which are generally lower than in northern Chinese aerosols. This indicates that human activities have little impact on the atmosphere in this area. However, high enrichment factors (greater than 10) for heavy metals found in Muztagata dust aerosols indicate their partly anthropogenic contributions.

Seasonal variations in heavy metal concentrations are pronounced in the Eastern Pamirs atmosphere. The seasonal variations of As, Cd, Zn, Bi and Pb resemble that of the crustal element Al, with high concentrations during summer and low during winter. Cu, Cr, and Ni have their own particular variations that differ from that of crustal Al. Back-trajectory investigations show that the anthropogenic pollution source areas lie in West, Central, and South Asia, and any of them can cause high heavy metal concentrations or EF values.

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